

PREPARATION AND REACTIVITY OF LATEXES FROM LOW-RANK COALS

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INTRODUCTION

The conversion of coals into oils, solutions, or dispersions is of great interest in the production of new liquid fuels. This paper describes our investigations of the conversion of low-rank coals into a stable dispersed form which exhibits altered reactivities toward various alkylating, reducing, and oxidizing reagents. This stable dispersion of a solid in a liquid medium is properly called a latex.

Extraction of coal with aqueous base such as sodium hydroxide followed by precipitation by the addition of acid to the extract yields dark material known as humic acid. Humic acids are defined by van Krevelen (1) as plant-derived "components which can be 'dissolved' in alkaline hydroxide," while others regard humic acids as being the water- or base-extractable material formed from oxidation of coal (2). The term is used both for the products of the decay and gelification of woody material and the products from coal. Since the compositions of neither the oxidized or unoxidized material are well defined, we shall use the term in a general sense to mean the material recovered from acidification of base extracts, although the materials in this report were obtained by base treatments of unoxidized coals carried out in the absence of oxidizing reagents and oxygen. The low-rank coals are hydrophilic in nature owing to their high concentrations of carboxylic acid and hydroxyl groups, consequently they yield significantly greater amounts of humic acids than do the bituminous coals. The yields of humic acids from lignites are known to vary with temperature and base concentration and of course with the degree of oxidation before or during the extraction. Unoxidized North Dakota lignites generally give about 4% yields of humic acids in extractions with 5% sodium hydroxide at ambient temperatures in 12 hours. In contrast, leonardites are highly oxidized lignites and easily convert to humic acids in 80% to 90% yields (3).

The objective of this study was to study the conversion of low-rank coals to humic acids under conditions of high mass flow (under nitrogen) and to investigate the nature of the humate material with regard to solubility and reactivity. The effects of coal type, nature of the base, and added surfactant on the conversion were studied.

EXPERIMENTAL

Coal samples (10 g) were blended with 5% sodium hydroxide or other basic solution (250 ml) in a 1.25 l kitchen-style Osterizer placed in a large glove bag under nitrogen atmosphere. Low conversions were obtained at the medium speed blending for 12 hours, and high conversions were obtained at the high speed for 2 hours. The temperature of the medium rose to about 45°C during the extraction as a result of blade friction. The blended slurry was washed into 250 ml centrifuge bottles and centrifuged at 3000 rpm in an IEC Model K centrifuge. The supernatant latex was then carefully decanted from the residue. Analytical data for the coals are presented in Table 1.

TABLE 1
ANALYTICAL DATA FOR LOW-RANK COALS

Analysis	Beulah Lignite	Wyodak Sub	Big Brown Lignite
Moisture	28.8	30.4	27.8
Volatile Matter	29.0	30.5	32.8
Fixed Carbon	30.8	33.2	30.0
Ash	11.7	5.8	9.5
Carbon, maf	69.5	73.5	69.9
Hydrogen, maf	4.4	5.2	5.2
Nitrogen, maf	1.0	1.1	1.2
Sulfur, maf	2.8	0.7	1.2
Oxygen (dif), maf	22.3	19.5	22.4

RESULTS AND DISCUSSION

Treatment of low-rank coals with aqueous basic solutions in the blender under nitrogen atmosphere and very mild temperatures (45°C) gave high conversions to products which were stable to centrifugation. The residue of larger particles which did separate during centrifugation was examined by photoacoustic FTIR spectroscopy and microscopic petrographic techniques and was found to consist mainly of minerals and liptinite macerals. The black suspension obtained after centrifuging and decanting from the residue resembled the black humate "solution" obtained in 4% yield by the simple sodium hydroxide extraction of lignites. The latex was examined in a static cell of a low-angle laser light scattering photometer. An intense flashing or sparkling characteristic of fine particle or colloidal suspensions (Tyndall effect) was observed. This contrasts with the glowing spot of Raleigh scattered light observed for methyl and acetylated derivatives of the humic acids which are highly soluble in organic solvents such as toluene, tetrahydrofuran, and dimethylformamide (3).

Addition of acid to the latex resulted in precipitation of the humic acid. Conversions were determined from weight yields of the precipitated humic acids after drying and are reported in Table 2. Addition of the acid was presumed to neutralize the negative charges of the carboxylate and phenolate anions of the colloidal coal particles by converting them to the acid and phenol forms. Coagulation of the particles occurred when the pH was lowered to about 4, where repulsive forces of the remaining carboxylate anionic groups no longer overcome the attractive forces between the coal macromolecules.

The highest conversions to the latex were observed for the Beulah (North Dakota) lignite where a 90% yield of humic acids was obtained by blending at high speed with 5% sodium hydroxide. This contrasts with the 28% yield obtained at medium speed blending of the same coal. It is believed that the high-speed stirring is required to increase the mass flow of aqueous base through the coal pore structure.

The effect of the nature of the base used in the blender treatment was investigated. When a 5% sodium carbonate solution was used, a 27% conversion of the Beulah lignite was obtained. The lower yield for this base suggests that high concentrations of hydroxide, as well as the high mass flow, may be essential for effective

TABLE 2
CONVERSIONS OF LOW-RANK COALS TO LAXTEXES

Coal	Blender Speed	Base	Yield of Humic Acid (Wt.% mf)
Beulah	high	NaOH	90
Beulah	med	NaOH	28
Beulah	mag.stir.	NaOH	4
Beulah	high	Na ₂ CO ₃	27
Beulah	high	NH ₄ OH	11
Beulah	high	pyridine	7
Beulah	high	NaOCH ₃	3
Wyodak	high	NaOH	65
Big Brown	high	NaOH	81

production of the latex. The use of sodium carbonate offers the possibility of easier recovery of humic acids from the latex using carbon dioxide to lower the pH and then regeneration of the sodium carbonate solution by heating the recovered aqueous phase. The lower conversion to the latex form using sodium carbonate may be compensated by its ease of regeneration and thus may be useful in coal cleaning or liquefaction processing of low-rank coals. Ammonium hydroxide (30%) gave a conversion of 11%. Thus a mechanism involving nucleophilic attack by the base does not seem to be important. Pyridine (neat) gave only a 7% conversion.

When the reaction of dried lignite with sodium methoxide in methanol was carried out with high-speed blending, the conversion was insignificant. Essentially only the waxy acids and some hydrocarbons were solubilized. Photoacoustic spectroscopy of the coal residue showed no incorporation of the methanol as methyl esters or ethers. A nucleophilic role of the base in the blending process again does not seem likely. Since transesterification was not exhibited in this attempted reaction with methoxide in methanol, it is unlikely that hydroxide would act by an equivalent ester hydrolysis mechanism in the aqueous hydroxide medium. No evidence exists for the presence of a significant amount of esters in low-rank coals. A possible mechanism for the aqueous hydroxide reaction is the base-catalyzed guaiacol ether cleavage demonstrated for lignin. The low-rank coals have small amounts of guaiacols and presumably some residual lignin. Cleavage of the alpha (benzyl) ethers of these residual and, therefore, hindered structures may require the high hydroxide concentrations and high mass flow conditions which we know to be important for breakdown to the colloidal state. Breakage of hydrogen bonds may also be important. The creation of a highly charged surface essential to the colloidal formation was clearly not possible in the blending attempt in methanol but was obtainable in water.

Two other coals were investigated for comparison with the Beulah (North Dakota) lignite. Wyodak subbituminous coal gave a conversion of 65% with high-speed blending in 5% sodium hydroxide. A Big Brown (Texas) lignite sample in the same conditions gave a conversion of 81%. The reason for the lower conversions of these two coals is not yet understood, but these two coals are known to be more aliphatic and contain less lignin than the Beulah lignite, which gave a 90% conversion.

The latexes from the Beulah lignite were shown to be quite reactive to alkylating reagents. Dimethyl sulfate was added to the aqueous basic latexes to give the methyl humate derivatives. These products were soluble in organic solvents, but insoluble in water. The molecular weights of these soluble derivatives were determined using low-angle laser light scattering photometry after reduction with zinc metal (4). These results indicate that the more severe blending processing breaks more of the cross-links or branch-points in the coal structure to give the higher yields of humic acids but in a smaller size distribution (Table 3) (5). The reactivities of the latexes in oxidizing and reducing conditions are currently under investigation.

TABLE 3
MOLECULAR WEIGHTS OF REDUCED METHYL HUMATE DERIVATIVES

Source of Humate Derivative	M_w (daltons)
High speed blending (90% yield)	4.3×10^5
Medium speed blending (28% yield)	8.8×10^5
Mag. stirring (4% yield)	1.3×10^6

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